The original Renner-Teller effect

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Abstract

In his classic paper R. Renner [Z. Phys. **92**, 172 (1934)] considered electronically excited CO_2 as an example of an open-shell linear triatomic molecule. Linear triatomic molecules have a doubly degenerate bending vibration. Renner was the first to study the effect of the electronic motion on the bending vibrational wave functions. For a Σ electronic (ground) state there is no coupling of the electronic motion with vibration, for a Π electronic state there is appreciable coupling, while the magnitude of the couplings with Δ ($\Lambda = 2$), Φ ($\Lambda = 3$), ..., electronic states, decreases steeply as function of electronic angular momentum Λ (in the model of Renner). Renner did not consider electron spin or the rotation of the triatom. In this report Renner's arguments will be summarized.

Introduction

In 1933 Gerhard Herzberg and Edward Teller [Z. Phys. Chemie **B21**, 410 (1933)] recognized that the potential of a triatomic linear molecule in a degenerate electronic state splits into two when the molecule is bent. A year later this effect was worked out in detail by Rudolf Renner, who gave an explanation of this splitting and showed that the bending and electronic motion are coupled. He predicted that this coupling would give rise to anomalies in the vibrational side bands of electronic spectra. Herzberg refers to this as the "Renner-Teller" effect in one of his influential books [*Molecular Spectra and Molecular Structure* Vol. III, Reprint Edition, Krieger, Malabar (1991)] and consequently the effect is now generally called after Renner and Teller, although it would be more appropriate to speak of the "Renner-Herzberg" or "Renner-Herzberg-Teller" effect as Herzberg was the first author on the 1933 paper.

In its simplest form the Renner-Teller effect occurs in open-shell linear triatomic molecules. Let the electronic state $|\,\Lambda\,\rangle$ be an eigenstate of L_z^{el}, the projection of the electronic angular momentum operator on the molecular axis, with eigenvalue $\hbar\Lambda$. The states $|\,\pm\Lambda\,\rangle$ are degenerate with energy $E_{|\Lambda|}^{\mathrm{el}}$. Let $|\,v, l\,\rangle$ be a harmonic bending vibration function, which is an eigenfunction of L_z^{vib}, the projection of the vibrational angular momentum operator on the molecular axis, with eigenvalue $\hbar l$. The $v + 1$ states

$|\, v, l \,\rangle,\ \ l = -v, -v+2, \ldots, v$ are degenerate with energy $h\nu(v+1)$. The orthonormal product states

$$|\, 1 \,\rangle \equiv |\, \Lambda \,\rangle \otimes |\, v, K-\Lambda \,\rangle \ \text{ and } \ |\, 2 \,\rangle \equiv |\, -\Lambda \,\rangle \otimes |\, v, K+\Lambda \,\rangle$$

are eigenfunctions of

$$L_z^{\mathrm{tot}} \equiv L_z^{\mathrm{el}} \otimes 1 + 1 \otimes L_z^{\mathrm{vib}} \tag{1}$$

with eigenvalue $\hbar K$. In zeroth-order the product kets are degenerate with energy $E^{\mathrm{el}}_{|\Lambda|} + h\nu(v+1)$. The bending of the molecule generates a coupling between the electronic and vibrational motion (a so-called vibronic coupling) that acts as a perturbation. Diagonalization of the 2×2 matrix of this perturbation on basis of $|\, 1 \,\rangle$ and $|\, 2 \,\rangle$ gives two new orthonormal zeroth-order eigenvectors $\psi_+^{(0)} = \cos\alpha |\, 1 \,\rangle + \sin\alpha |\, 2 \,\rangle$ and $\psi_-^{(0)} = -\sin\alpha |\, 1 \,\rangle + \cos\alpha |\, 2 \,\rangle$ with first order energies: $E^{(1)}_{\pm}$. Clearly, the functions $\psi_\pm^{(0)}$ are no longer simple products; this breakdown of the Born-Oppenheimer approximation is the Renner-Teller effect. Also belonging to the Renner-Teller effect is the observation that the functions $\psi_\pm^{(0)}$ are not degenerate in first order. The linear combinations $\psi_\pm^{(0)}$ are not eigenfunctions of L_z^{el} or L_z^{vib}. However, they are eigenfunctions of L_z^{tot}.

Much has been published about the Renner-Teller effect after its first experimental observation in 1959. Nowadays, authors referring to this effect have usually broader physical phenomena and larger molecules in mind than Renner had in 1934. For instance, Bunker and Jensen [*Molecular Symmetry and Spectroscopy*, NRC Research Press, Ottawa (1998)] very specifically state that the effect is not only due to the coupling of electrons and vibrations, but also to coupling with rotations—a rovibronic effect. Examples they quote are linear 5- and 6-atom molecules such as HC_3N and HC_4H^+.

It is of interest, historically and scientifically, to recall the content and scope of the original Renner paper. Renner's paper is well accessible due to the English translation by H. Hettema [*Quantum Chemistry: Classic Scientific Papers*, World Scientific, Singapore (2000)]. Renner's work will be rephrased in modern language and condensed in this report. A knowledge of the theory of the 2-dimensional harmonic oscillator is presupposed in Renner's paper and since we do not want to assume this we start with a short exposition of the 2D oscillator. Then we will give a resumé of Renner's work. In doing this, we will sometimes modify the original arguments somewhat, but we will indicate this, either in the text or in a footnote.

The 2-dimensional harmonic oscillator

The Hamiltonian of the 2-D isotropic harmonic oscillator is

$$H_v = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)+\frac{1}{2}(x^2+y^2)\,f,$$

where μ is the (reduced) mass, f is the force constant and $\hbar$ is Planck's constant divided by 2π. Multiply left and right hand side of the corresponding eigenvalue equation by $\gamma \equiv 1/\hbar\sqrt{\mu/f}$, substitute $r \rightarrow (\mu f/\hbar^2)^{1/4} r$ and it becomes

$$H_v\Psi \equiv \left[-\frac{1}{2}\Big(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\Big)+\frac{1}{2}(x^2+y^2)\right]\Psi = E\Psi,$$

where E is in units $\gamma^{-1} = \hbar\sqrt{f/\mu}$. As is well-known, the eigenvalue equation of H_v factorizes into an x and a y part:

$$\begin{aligned} -\frac{1}{2}\left(\frac{\partial^2}{\partial x^2}-x^2\right)\psi_{n_x}(x) &= (n_x+\frac{1}{2})\psi_{n_x}(x) && (2)\\ -\frac{1}{2}\left(\frac{\partial^2}{\partial y^2}-y^2\right)\psi_{n_y}(y) &= (n_y+\frac{1}{2})\psi_{n_y}(y), && (3)\end{aligned}$$

where n_x and n_y are natural numbers and the total energy is $v+1$, with $v \equiv n_x + n_y$. In polar coordinates

$$\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} r\cos\varphi \\ r\sin\varphi \end{pmatrix},$$

H_v becomes:

$$H_v = T_v + \frac{1}{2}r^2 \qquad (4)$$

with

$$T_v = -\frac{1}{2}\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\right). \qquad (5)$$

Substitute $\psi_v(r,\varphi) = e^{il\varphi}R(r)$ into $H_v\psi_v = (v+1)\psi_v$ and we get for the r-dependent part

$$\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}-\frac{l^2}{r^2}-r^2+2(v+1)\right)R(r) = 0. \qquad (6)$$

Recall that periodicity in φ requires l to be integer. By three substitutions the equation in r can be transformed into the associated Laguerre differential equation [see, *e.g.*, H. Margenau and G. M. Murphy, *The Mathematics of*

Physics and Chemistry, Van Nostrand, New York, 2nd Ed. (1964)]. First we substitute $R(r) = r^l \exp(-r^2/2) L(r)$ ($l \geq 0$), which gives a differential equation for $L(r)$,

$$\frac{\partial^2 L(r)}{\partial r^2} + \frac{\partial L(r)}{\partial r}\left(-2r + \frac{2l+1}{r}\right) + L(r)(2v - 2l) = 0.$$

Next substitute $x = r^2$, then

$$x\frac{\partial^2 L(x)}{\partial x^2} + \frac{\partial L(x)}{\partial x}(l + 1 - x) + L(x)\frac{(v-l)}{2} = 0.$$

Substitute finally $n = (v + l)/2$ and $k = l$, so that we get

$$x\frac{\partial^2 L(x)}{\partial x^2} + \frac{\partial L(x)}{\partial x}(k + 1 - x) + L(x)(n - k) = 0,$$

which has as solutions the associated Laguerre polynomials

$$L_n^k(x) = \frac{d^k}{dx^k} L_n(x) \text{ with } n = 0, 1, 2, \ldots \text{ and } k \leq n.$$

Here $L_n(x)$ is an ordinary Laguerre polynomial of order n. In summary,

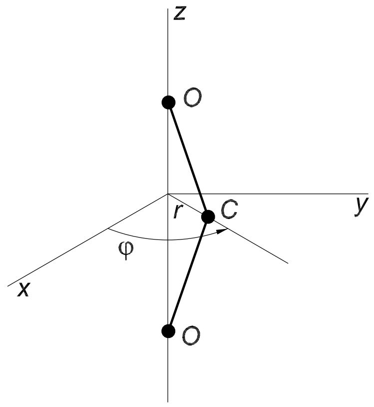
$$\psi_v(r, \varphi) = e^{il\varphi} r^{|l|} \ \exp(-r^2/2) \ L^{|l|}_{(v+|l|)/2}(r^2)$$

is an (unnormalized) eigenfunction of H_v with eigenvalue $v+1$, $v = 0, 1, 2, \ldots$. Further $|l| \leq v$ and $l = -v + 2n$, so that $l = -v, -v + 2, \ldots, v - 2, v$. The vibrational angular momentum quantum number l labels the $v+1$ degenerate states. Also for fixed l: $v = |l|, |l| + 2, |l| + 4, \ldots$. Renner uses the notation $R_{Nm}(r)$ for the radial part of these solutions, with $m \leftrightarrow |l|$ and $R_{Nm}(r) \equiv L^m_{(N+m)/2,m}(r^2)$, so that $N \leftrightarrow v$.

Electron-vibration coupling according to Renner

Of course, even an approximate solution of the electronic Schrödinger equation for a molecule of the size of CO_2 was completely out of reach in 1934. Renner had to make many simplifications and to use intuitive arguments to obtain the required coupling terms. The simplifications he made are the following: the molecule does not rotate or translate. The C–O symmetric and antisymmetric stretching vibrations are completely decoupled from the doubly degenerate bending. The electronic wave function is an orbital (a function of *one* electron). The molecule is bent as shown in Fig. 1. We write the spherical polar coordinates of the electron as $\boldsymbol{q} = (\rho, \beta, \theta)$, where θ is the

Figure 1: *Bending coordinates in the molecule* CO_2



azimuthal (rotation around z-axis) angle and ρ is the distance of the electron to the origin. In a linear molecule the orbitals

$$\psi^{I}(\boldsymbol{q}) = f(\rho,\beta)\cos\Lambda(\theta-\varphi) \tag{7}$$
$$\psi^{II}(\boldsymbol{q}) = f(\rho,\beta)\sin\Lambda(\theta-\varphi) \tag{8}$$

are degenerate, where Λ is a natural number. The orbital $\psi^{I}(\boldsymbol{q})$ is symmetric under reflection in the plane of the distorted molecule in Fig. 1, while $\psi^{II}(\boldsymbol{q})$ is antisymmetric under the same reflection. Note that these electronic orbitals contain explicitly the nuclear coordinate φ. In the one-electron case $L_z^{\text{el}} = -i\hbar\partial/\partial\theta$ and $L_z^{\text{vib}} = -i\hbar\partial/\partial\varphi$. Clearly,[1] the orbitals are eigenfunctions with $K = 0$ of L_z^{tot} defined in Eq. (1). Renner now makes the crucial assumption that these orbitals are eigenfunctions of a clamped nuclei effective one-electron Hamiltonian[2] H_e, even in the case of (small) bending, and writes

$$H_e\psi^{I}(\boldsymbol{q}) = (E_\Lambda + \sigma(r))\psi^{I}(\boldsymbol{q}) \tag{9}$$
$$H_e\psi^{II}(\boldsymbol{q}) = (E_\Lambda - \sigma(r))\psi^{II}(\boldsymbol{q}), \tag{10}$$

here E_Λ is the energy of the two orbitals in the linear ($r = 0$) case. The two orbital energies lie symmetrically with regard to E_Λ. Later in the paper it is assumed that $\sigma(r) \geq 0$ for all r, so that the antisymmetric orbital is lower in energy than the symmetric one.

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[1] Renner did not see the angular momentum aspect of his work too clearly. His "Gesamtdrehimpuls" (total angular momentum) refers to vibrational coordinates only.

[2] Renner writes out a full N-electron Hamiltonian H_e and calls the single electron that he considers consequently the "first" electron

To evaluate $\sigma(r)$, Renner assumes that the bending introduces a vibrational dipole moment $\mu_{\rm nuc} = er$ located at the origin and that the electron at position $\boldsymbol{q}$ interacts with this dipole. He approximates the usual charge-dipole interaction $\boldsymbol{q} \cdot \boldsymbol{\mu}_{\rm nuc}/\rho^3$ by $U = er\cos(\theta - \varphi)/\rho^2$ and sets up a matrix[3] of this vibronic interaction on basis of the functions (7) and (8). The perturbation matrix decomposes into two blocks, one on basis of the sine functions and the other on basis of the cosine functions, because

$$\langle\, \psi^I \mid \cos(\theta - \varphi) \mid \psi^{II} \,\rangle = 0.$$

The matrix elements are taken to be proportional to

$$\int_0^{2\pi} \cos\Lambda'\theta' \cos\theta' \cos\Lambda\theta' d\theta' \;\; = \;\; \int_0^{2\pi} \sin\Lambda'\theta' \cos\theta' \sin\Lambda\theta' d\theta' = \frac{\pi}{2},$$

with $\theta' \equiv \theta - \varphi$, $\Lambda', \Lambda > 0$, and $\Lambda' = \Lambda \pm 1$. There is a common proportionality constant, which is an integral over the remaining electron coordinates. Since the matrix elements vanish unless $\Lambda' = \Lambda \pm 1$, the two blocks are tridiagonal and its elements are all equal, except for the case $\Lambda' = 0$ (Σ) and $\Lambda = 1$ (Π) in the cosine block, where the value is π. The same matrix element is zero in the sine block. If the two blocks were identical, the perturbation would shift sine and cosine orbitals by the same amount and their degeneracy would not be lifted. However, the blocks differ in the single matrix element $\langle\, \Sigma \mid \cos(\theta - \varphi) \mid \Pi \,\rangle$, which implies that the cosine orbitals shift differently than the sine orbitals. By applying second-order perturbation theory Renner shows that the energy of $\cos(\theta - \varphi)$ shifts in second order in U, i.e., the splitting between the cosine and sine Π orbital is quadratic in r. Similarly the Δ orbitals split in fourth order (energy difference is quartic in r), etc. Renner then argues that only the case $\Lambda = 1$ is of physical interest and considers subsequently only the second-order (in U) electronic energy splitting

$$\sigma(r) = \sigma r^2 \tag{11}$$

as part of the vibronic coupling and restricts his attention to orbitals [Eqs. (7) and (8)] with $\Lambda = 1$ only. The positive constant σ enters the theory as a free parameter. Often the splitting of the Π orbital energy upon bending is referred to as the Renner effect, but the description of this effect is only a prelude to the study of the effect of the Π splitting on the bending vibrational energies.

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[3] Here and in the calculation of the perturbation matrix Renner sets $\varphi = 0$

The Renner equations

Since we have here a case of two close lying potential energy surfaces, coinciding for $r = 0$, the usual single-product Born-Oppenheimer Ansatz will not do. Instead Renner makes the inner product Ansatz

$$\psi_{\text{tot}}(\boldsymbol{q}, r, \varphi) = \left(\psi^I(\boldsymbol{q}), \psi^{II}(\boldsymbol{q})\right) \begin{pmatrix} \psi^I(r,\varphi) \\ \psi^{II}(r,\varphi) \end{pmatrix} \tag{12}$$

where $\psi^I(\boldsymbol{q})$ and $\psi^{II}(\boldsymbol{q})$ are the eigenfunctions of H_e, the effective one-electron Hamiltonian appearing in Eqs. (9) and (10). In this subsection we will derive coupled equations from which $\psi^I(r,\varphi)$ and $\psi^{II}(r,\varphi)$ may be solved. We refer to these equations as the "Renner equations".

The total vibronic Hamiltonian is

$$H_{\text{tot}} = H_e + H_v \tag{13}$$

with

$$H_v = T_v + \alpha r^2 \text{ and } T_v = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2}\right), \tag{14}$$

and where $\alpha = \frac{1}{2}f$. Following Renner, we consider only the case $\Lambda = 1$ and write $E_\pi \equiv E_{\Lambda=1}$. Substitute Eq. (12) into the eigenvalue equation $H_{\text{tot}}\psi_{\text{tot}} = E_{\text{tot}}\psi_{\text{tot}}$ [cf. also Eqs. (7) and (8)]:

$$\begin{aligned} H_{\text{tot}}\psi_{\text{tot}} &= f(\rho,\beta)(E_\pi + \sigma r^2)\cos(\theta-\varphi)\psi^I(r,\varphi) \\ &+ f(\rho,\beta)(E_\pi - \sigma r^2)\sin(\theta-\varphi)\psi^{II}(r,\varphi) \\ &+ f(\rho,\beta)H_v\cos(\theta-\varphi)\psi^I(r,\varphi) \\ &+ f(\rho,\beta)H_v\sin(\theta-\varphi)\psi^{II}(r,\varphi) \\ &= E_{\text{tot}} f(\rho,\beta)\left[\cos(\theta-\varphi)\psi^I(r,\varphi) + \sin(\theta-\varphi)\psi^{II}(r,\varphi)\right]. \end{aligned}$$

Here we assumed that $H_v f(\rho,\beta) = f(\rho,\beta)H_v$, i.e., that the parametric dependence of $f(\rho,\beta)$ on the nuclear coordinates r and φ is weak. Define

$$\begin{aligned} \widetilde{T}_v &\equiv -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2} - \frac{1}{r^2}\right) \\ p_\varphi &\equiv -\frac{\hbar^2}{\mu r^2}\frac{\partial}{\partial\varphi} \end{aligned}$$

then

$$\begin{aligned} T_v\cos(\theta-\varphi)\psi^I(r,\varphi) &= \cos(\theta-\varphi)\widetilde{T}_v\psi^I(r,\varphi) + \sin(\theta-\varphi)p_\varphi\psi^I(r,\varphi) \\ T_v\sin(\theta-\varphi)\psi^{II}(r,\varphi) &= \sin(\theta-\varphi)\widetilde{T}_v\psi^{II}(r,\varphi) - \cos(\theta-\varphi)p_\varphi\psi^{II}(r,\varphi). \end{aligned}$$

The eigenvalue equation of H_{tot} can be written as

$$\begin{aligned} & \cos(\theta-\varphi)\left[\left(\widetilde{T}_v+(\alpha+\sigma)r^2\right)\psi^I(r,\varphi)-p_\varphi\psi^{II}(r,\varphi)\right] \\ + \; & \sin(\theta-\varphi)\left[\left(\widetilde{T}_v+(\alpha-\sigma)r^2\right)\psi^{II}(r,\varphi)+p_\varphi\psi^I(r,\varphi)\right] \\ = \; & E\cos(\theta-\varphi)\psi^I(r,\varphi)+E\sin(\theta-\varphi)\psi^{II}(r,\varphi), \end{aligned}$$

where we defined $E = E_{\text{tot}} - E_\pi$ and divided out $f(\rho,\beta)$. Equating the factors of $\cos(\theta-\varphi)$ and of $\sin(\theta-\varphi)$, we get the coupled equations for the vibrational functions ψ^I and ψ^{II}:

$$\underbrace{\begin{pmatrix} \widetilde{T}_v+(\alpha+\sigma)r^2 & -p_\varphi \\ +p_\varphi & \widetilde{T}_v+(\alpha-\sigma)r^2 \end{pmatrix}}_{\widehat{\mathbb{H}}} \begin{pmatrix} \psi^I(r,\varphi) \\ \psi^{II}(r,\varphi) \end{pmatrix} = E \begin{pmatrix} \psi^I(r,\varphi) \\ \psi^{II}(r,\varphi) \end{pmatrix}. \qquad (15)$$

These equations may be transformed to exponential basis; the total vibronic wave function is invariant under such a transformation,

$$\psi_{\text{tot}}(\boldsymbol{q},r,\varphi) = \frac{1}{2}\left(\psi^I(\boldsymbol{q}),\psi^{II}(\boldsymbol{q})\right)\begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix}\begin{pmatrix} \psi^I(r,\varphi) \\ \psi^{II}(r,\varphi) \end{pmatrix}.$$

If $\sigma = 0$ the orbitals $\psi^I(\boldsymbol{q})$ and $\psi^{II}(\boldsymbol{q})$ are degenerate and then we may as well depart from

$$\widetilde{\psi}^I(\boldsymbol{q}) = f(\rho,\beta)e^{i(\theta-\varphi)} \qquad (16)$$

$$\widetilde{\psi}^{II}(\boldsymbol{q}) = f(\rho,\beta)e^{-i(\theta-\varphi)} \qquad (17)$$

instead of from Eqs. (7) and (8). This has the advantage that the off-diagonal elements in Eq. (15) are moved to the diagonal. These off-diagonal elements are due to the fact that the first derivative of a sine (cosine) is a cosine (sine), while the first derivative of an exponential is an exponential. The coupled equations uncouple (for $\sigma = 0$) and both become a harmonic oscillator equation in polar coordinates. Hence, we consider the following transformation of Eq. (15)

$$\frac{1}{2}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix}\widehat{\mathbb{H}}\begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix}\begin{pmatrix} \psi^I \\ \psi^{II} \end{pmatrix} = E\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix}\begin{pmatrix} \psi^I \\ \psi^{II} \end{pmatrix}.$$

Or,

$$\boxed{\begin{pmatrix} \widetilde{T}_v+\alpha r^2-ip_\varphi & \sigma r^2 \\ \sigma r^2 & \widetilde{T}_v+\alpha r^2+ip_\varphi \end{pmatrix}\begin{pmatrix} \widetilde{\psi}^I(r,\varphi) \\ \widetilde{\psi}^{II}(r,\varphi) \end{pmatrix} = E\begin{pmatrix} \widetilde{\psi}^I(r,\varphi) \\ \widetilde{\psi}^{II}(r,\varphi) \end{pmatrix}} \qquad (18)$$

with

$$\begin{pmatrix} \widetilde{\psi}^{I}(r,\varphi) \\ \widetilde{\psi}^{II}(r,\varphi) \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix} \begin{pmatrix} \psi^{I}(r,\varphi) \\ \psi^{II}(r,\varphi) \end{pmatrix}. \tag{19}$$

Although Renner does not give Eqs. (18) explicitly, they may be justifiably called the *Renner equations*; they are completely equivalent with Eqs. (15), which *are* given by Renner. We reiterate that the two parameters in this equation: α (twice the force constant) and σ (twice the splitting of the Π orbitals due to bending) are free parameters.

Approximate solution of the Renner equations

Renner solves his equations by perturbation theory and finds two closely related solutions for each angular momentum quantum number M.

The zeroth order equations arise for $\sigma = 0$:

$$\begin{aligned} \left(\widetilde{T}_v + \alpha r^2 - ip_\varphi\right) \widetilde{\psi}^{I}(r,\varphi) &= E^{(0)} \widetilde{\psi}^{I}(r,\varphi) \\ \left(\widetilde{T}_v + \alpha r^2 + ip_\varphi\right) \widetilde{\psi}^{II}(r,\varphi) &= E^{(0)} \widetilde{\psi}^{II}(r,\varphi). \end{aligned}$$

Substituting

$$\begin{aligned} \widetilde{\psi}^{I} &= e^{i\varphi}\phi^{I}(r,\varphi) \\ \widetilde{\psi}^{II} &= e^{-i\varphi}\phi^{II}(r,\varphi) \end{aligned}$$

and using

$$\left[\frac{\partial^2}{\partial\varphi^2} \mp 2i\frac{\partial}{\partial\varphi} - 1\right] e^{\pm i\varphi}\phi(r,\varphi) = e^{\pm i\varphi}\frac{\partial^2\phi(r,\varphi)}{\partial\varphi^2}$$

we get for both $\phi^{I}(r,\varphi)$ and $\phi^{II}(r,\varphi)$ the 2D-harmonic oscillator equation

$$(T_v + \alpha r^2)\phi(r,\varphi) = E^{(0)}\phi(r,\varphi),$$

with T_v given in Eq. (14). Hence, not surprisingly, the zeroth-order functions are the harmonic oscillator functions studied above where we denoted the vibrational angular momentum quantum number by l and the vibration quantum number by v. Renner uses $m \ge 0$ and N, respectively, and writes the total vibrational wave function as $\exp(\pm im\varphi)R_{Nm}(r)$. Recall that the energy $h\nu(N+1)$ is $N+1$ fold degenerate, where $2\pi\nu = \sqrt{2\alpha/\mu}$. We have now the 2×2 operator perturbation

$$\widehat{\mathbb{W}} = \begin{pmatrix} 0 & \sigma r^2 \\ \sigma r^2 & 0 \end{pmatrix}$$

and the corresponding zeroth-order functions

$$\begin{aligned} \mid 1, N, M \,\rangle &\equiv e^{i\varphi} e^{i(M-1)\varphi} R_{N,M-1}(r) \\ \mid 2, N, M \,\rangle &\equiv e^{-i\varphi} e^{i(M+1)\varphi} R_{N,M+1}(r). \end{aligned}$$

Here the respective quantum numbers m are chosen such that both functions are an eigenfunction of L_z^{tot} with eigenvalue M. The full solutions are the degenerate two-component wave functions

$$\Psi_1 \equiv \begin{pmatrix} \mid 1, N, M \,\rangle \\ 0 \end{pmatrix} \text{ and } \Psi_2 \equiv \begin{pmatrix} 0 \\ \mid 2, N, M \,\rangle \end{pmatrix}. \tag{20}$$

The (i, j) element of the perturbation matrix is

$$V_{ij} = \langle\, \Psi_i \,|\widehat{\mathbb{W}}|\, \Psi_j \,\rangle,$$

for instance,

$$V_{12} = \Big(\langle\, 1, N, M \mid,\ 0 \Big)\, \widehat{\mathbb{W}} \begin{pmatrix} 0 \\ \mid 2, N, M \,\rangle \end{pmatrix} = \langle\, 1, N, M \mid \sigma r^2 \mid 2, N', M \,\rangle.$$

Since the perturbation matrix consists of 2×2 blocks labeled by M, N and N', we define

$$\mathbb{V}_M^{NN'} \equiv \begin{pmatrix} 0 & a_M^{NN'} \\ b_M^{NN'} & 0 \end{pmatrix} \tag{21}$$

with

$$\begin{aligned} a_M^{NN'} &\equiv \langle\, 1, N, M \mid \sigma r^2 \mid 2, N', M \,\rangle \\ b_M^{NN'} &\equiv \langle\, 2, N, M \mid \sigma r^2 \mid 1, N', M \,\rangle. \end{aligned}$$

Clearly the φ-dependent part of matrix elements of r^2 on basis of $\mid i, N, M \,\rangle$ gives $\delta_{M,M'}$. Recall that in the function $R_{Nm}(r)$ we have $|m| \leq N$, so that for $\mid 1, N, M \,\rangle$ holds $N \geq |M-1|$ and for $\mid 2, N, M \,\rangle$ holds $N \geq |M+1|$. Consequently incomplete blocks appear at the border of the perturbation matrix. As an example consider $M = 3$, $N = 2$, and $N' = 4$. Then bra and ket in $\langle\, 1, 2, 3 \mid \sigma r^2 \mid 2, 4, 3 \,\rangle$ exist, while in the corresponding matrix element $\langle\, 2, 2, 3 \mid \sigma r^2 \mid 1, 4, 3 \,\rangle$ the bra does not exist.[4]

Matrix elements of the perturbation r^2 are easily calculated. Renner squared the matrix of r computed on basis of harmonic oscillator functions. The presence of Kronecker delta's gives the matrix of r a very regular and

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[4] Renner erroneously interchanged superscripts 1 and 2 in his matrices.

sparse structure, so that the matrix multiplication can be done in closed form.

As pointed out by Renner, one does not need to apply perturbation theory for the $M = 0$ case, because then the wave function does not depend on φ and Eqs. (15) become the radial part of the harmonic oscillator equation, [cf. Eq. (6) with $l = 1$] with respective eigenvalues

$$E^{\pm}_{N,0} = \frac{\hbar}{\sqrt{\mu}}\sqrt{2(\alpha \pm \sigma)}(N+1) = \hbar(N+1)\sqrt{\frac{2\alpha}{\mu}}\sqrt{1 \pm \epsilon} = h\nu(N+1)\sqrt{1 \pm \epsilon},$$

with $N = 1, 2, 3 \ldots$. Here we introduced the Renner parameter ϵ, the quotient of splitting parameter σ and the force constant $\alpha \equiv f/2$. Recall that the total vibronic energy $E_{\text{tot}} = E^{\pm}_{N,0} + E_{\pi}$, where E_{π} is the energy of the electronic Π state. The vibronic wave functions[5] belonging to the energies with upper sign are

$$\psi^{I}(\boldsymbol{q})\psi^{I}(r_+, \varphi) = f(\rho, \beta)\cos(\theta - \varphi)R_{N,1}(r_+),$$

with $r_+ = \left(2(\alpha + \sigma)\mu/\hbar^2\right)^{1/4} r$ and those belonging to the lower sign are

$$\psi^{II}(\boldsymbol{q})\psi^{II}(r_-, \varphi) = f(\rho, \beta)\sin(\theta - \varphi)R_{N,1}(r_-),$$

with $r_- = \left(2(\alpha - \sigma)\mu/\hbar^2\right)^{1/4} r$. The total vibronic wave functions are simple products with eigenvalue $M = 0$ of L^{tot}_z.

For the case $M \neq 0$ the perturbation matrix has the following structure (the cutoffs on the borders are not shown) with the 2×2 blocks given by Eq. (21)

$$\begin{pmatrix} \mathbb{V}^{11}_M & \mathbb{V}^{12}_M & \mathbb{V}^{13}_M & \cdots \\ \mathbb{V}^{21}_M & \mathbb{V}^{22}_M & \cdots & \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

Renner diagonalizes the 2×2 blocks on the diagonal ($N = N'$)

$$\frac{1}{2}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}\begin{pmatrix} 0 & a^{NN}_M \\ a^{NN}_M & 0 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} = \begin{pmatrix} -a^{NN}_M & 0 \\ 0 & a^{NN}_M \end{pmatrix},$$

with $a^{NN}_M = b^{NN}_M = \sigma\sqrt{(N+M+1)(N-M+1)}$. The matrix element a^{NN}_M is proportional to the first-order energy $E^{(1)}$. The proportionality constant may be obtained by scaling r by $(2\alpha\mu/\hbar^2)^{1/4}$. Of course, also the off-diagonal blocks of the perturbation matrix are affected by this transformation. The

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[5] These wave functions are *not* given by Renner

new zeroth-order vibrational functions (not given by Renner) are (unnormalized)

$$\Psi_1 + \Psi_2 = \begin{pmatrix} |\, 1, N, M \,\rangle \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ |\, 2, N, M \,\rangle \end{pmatrix} = \begin{pmatrix} |\, 1, N, M \,\rangle \\ |\, 2, N, M \,\rangle \end{pmatrix}$$

and

$$\Psi_1 - \Psi_2 = \begin{pmatrix} |\, 1, N, M \,\rangle \\ -|\, 2, N, M \,\rangle \end{pmatrix}$$

with energies $\pm E^{(1)}$, respectively. The vibronic wave functions are [cf. Eqs. (16) and (17)]

$$\begin{aligned} \psi^{\pm}_{\text{tot}}(\boldsymbol{q}, r, \varphi) &= \left(\widetilde{\psi}^{I}(\boldsymbol{q}), \widetilde{\psi}^{II}(\boldsymbol{q})\right) \begin{pmatrix} |\, 1, N, M \,\rangle \\ \pm|\, 2, N, M \,\rangle \end{pmatrix} \\ &= f(\rho, \beta) \left(e^{i\theta} e^{i(M-1)\varphi} R_{N,M-1}(r) \pm e^{-i\theta} e^{i(M+1)\varphi} R_{N,M+1}(r) \right) . \end{aligned}$$

These two vibronic functions are no longer simple Born-Oppenheimer products of an electronic and a vibrational part, but are still eigenvectors of of L_z^{tot} with eigenvalue M. Note that the splitting of the energy proportional to $\pm\epsilon$ (the Renner-Teller effect) appears already in first order.

We will not follow Renner's second-order calculation in detail, because it is very specific and, moreover, the second-order energy does not give further splitting. Suffice it to say that the off-diagonal perturbation matrix elements are included by the well-known formula $E^{(2)}_{ii} = \sum_j |V_{ij}|^2/(E^{(0)}_i - E^{(0)}_j)$. In the corresponding first-order wave functions vibrational functions of different N are mixed (but M is conserved, as L_z^{tot} is a constant of the motion). The second-order energies depend quadratically on ϵ, so that they indeed give no further splitting.

We now copy Renner's results for $E^{\pm}_{NM}$, where ± refers to two solutions of the Renner equations. For $N = |M| + 2i - 1$, $|M| \neq 0$ and $i = 1, 2, \ldots$

$$E^{\pm}_{|M|+2i-1,M} = h\nu \left[|M| + 2i \pm \epsilon\sqrt{i(i + |M|)} - \frac{1}{8}\epsilon^2 (2i + |M|) \right] ,$$

and we note that the $\pm M$ states are degenerate, as is usual in the absence of magnetic fields. Note that the zeroth-order energy is $h\nu(|M| + 2i)$ and the remaining part is the first- and second-order correction due to the vibronic interaction $\pm\sigma r^2$.

For $i = 0$ and $M \neq 0$ there is no first-order energy, only second-order

$$E_{|M|-1,M} = h\nu \left[|M| - \frac{1}{8}\epsilon^2 |M|(|M| + 1) \right] ,$$

so that there is no $\pm\epsilon$ splitting here. This is to be expected since there is only one zeroth-order function with $N = |M| - 1$.

Epilogue

The Renner-Teller effect was not observed until 1959, when K. Dressler and D. A. Ramsay [Phil. Trans. Roy. Soc. London, **251A**, 553 (1959)] measured the electronic absorption spectrum of NH_2 and ND_2. They observed that the first electronically excited state has a linear geometry. In this excited state an unusual type of vibronic structure was found, which indicated that there is substantial electron-vibration coupling. This coupling was modeled by J. A. Pople and H. C. Longuet-Higgins, [who received the spectra before publication, see: Mol. Phys. **1**, 372 (1958)]. These workers extended the model of Renner by introducing anharmonicities and a $\cos 2(\theta - \varphi)$ coupling in the vibronic interactions. They set up the equivalent of matrix $\mathbb{V}_M^{NN}$ [see Eq. (21)] and assumed that $(1,1)/\sqrt{2}$ is an eigenvector. In this manner they got reasonable agreement with the spectra of Dressler and Ramsay. After this initial work many papers on the Renner-Teller effect have been published.

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